SEPARATION OF CRUDE OIL EMULSIONS VIA MICROWAVE HEATING TECHNOLOGY

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ABSTRACT

Enhancement of separation process involving liquid-liquid or solid-liquid can be achieved using microwave irradiation technology. The traditional ways of breaking emulsions include heating and chemical are disadvantageous both from economic and environmental perspectives. In this thesis, the microwave potentials in demulsification of water-in-crude oil emulsions are investigated. The study began with some characterization of w/o emulsions such as formation, formulation, stabilization and breaking of emulsions to provide fundamental understanding of crude oil emulsions. The aim was to obtain optimized operating conditions as well as fundamental understanding of water-in-oil emulsions, upon which further developments on demulsification processes can be developed. The stability studies were carried out by analyzing operating condition such as stirring time, surfactant concentration, temperature, water-oil ratios (50-50% and 20-80%) and agitation speed (500rpm,1000rpm and 1500rpm). Four emulsifiers namely: Span 80, Span 83, Cocamide MEA and Triton X-100 were used for w/o stabilizations. It was found that they exist a correlations between these factors and emulsion stability. For microwave power applied (720 watts, 540 watts and 360 watts), it conclude that the microwave power was proportional to the volume rate of heat generation and rate of temperature increase. Results show that microwave radiation can enhance the demulsification rate by order of magnitude. The result obtained in this study has exposed the capability of microwave technology in demulsification of water-in-oil emulsions. Further work is nevertheless required to provide deeper understanding of the mechanisms involved to facilitate the development of optimum system applicable to the industries.

ABSTRAK

Peningkatan pretasi proses pemisahan yang melibatkan cecair-cecair atau pepejal-cecair boleh dicapai dengan menggunakan teknologi penyinaran gelombang mikro. Cara-cara tradisional yang digunakan untuk memecahkan emulsi termasuk pemanasan dan penggunaan bahan kimia adalah kurang memuaskan dari segi ekonomi dan alam sekitar. Dalam kajian ini, potensi gelombang mikro pemisahan air dalam minyak mentah emulsi disiasat. Kajian ini bermula dengan pencirian beberapa emulsi air dalam minyak mentah seperti pembentukan, penggubalan, penstabilan, dan pembukaan emulsi untuk memberi kefahaman asas emulsi minyak mentah. Tujuannya adalah untuk mendapatkan keadaan operasi optimum serta memahami asas emulsi air dalam minyak, di mana perkembangan lanjut mengenai proses demulsification boleh dimajukan. Kajian kestabilan telah dijalankan dengan menganalisis keadaan operasi seperti kacau masa, kepekatan pengemulsi, suhu, nisbah air-minyak (50-50% dan 20-80%) dan kelajuan pergolakan (500rpm, 1000rpm dan 1500rpm). Empat pengemulsi iaitu: SPAN 80, SPAN 83, Cocamide MEA dan Triton X-100 telah digunakan untuk penyediaan emulsi stabil. Adalah didapati bahawa pembolehubah ini saling bergantung antara faktor-faktor ini dan kestabilan emulsi. Untuk penggunaan kuasa gelombang mikro (720 watt, 540 watt dan 360 watt), ia menyimpulkan bahawa kuasa gelombang mikro adalah berkadar dengan kadar jumlah penjanaan haba dan kadar kenaikan suhu. Keputusan menunjukkan bahawa radiasi gelombang mikro boleh meningkatkan kadar demulsification melalui perintah magnitud. Keputusan yang diperolehi dalam kajian ini telah mendedahkan keupayaan teknologi gelombang mikro dalam pemisahan air dari emulsi air dalam minyak. Kerja selanjutnya namun diperlukan untuk memberi kefahaman yang lebih mendalam tentang mekanisme yang terlibat bagi memudahkan pembangunan and penyelidikan sistem yang optimum yang diperlukankan oleh industri.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

A	Sample's container surface area
D	Diameter of water droplets
C_p	Heat capacity
D_p	Penetration depth
P_z	Microwave power transmitted
P_o	Microwave power flux
m	Mass of sample
q_{MW}	Rate of heat generation
$\tan \delta$	Loss tangent
v_w	Velocity of water
α_E	Attenuation factor
ε_r'	Dielectric constant
ε_r''	Dielectric Loss
λ_w	Wavelength
ρ_m	Density of emulsions
ρ_o	Density of oil
ρ_w	Density of water
μ_o	Viscosity of oil

LIST OF ABBREVIATIONS

O/W	Oil-in-water emulsion
W/O	Water-in-oil emulsion
W/O/W	Water-in-oil-in-water emulsion
PIT	Phase Inversion Temperature
Cocamide MEA	Cocamide monoethanolamine
Span 80	Sorbitan (Z)-mono-9-octadecenoate
Span 83	Sodium dodecyl sulphates
Triton X-100	Octylphenolpoly (ethyleneglycolether)$_x$

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Oil is world's major source of primary energy. It is used for a wide diversity of purposes ranging from fueling car to running machinery. When petroleum products are burned to produce energy, they may be used to propel a vehicle, as would be the case with gasoline, jet fuel, or diesel fuel; to heat a building, as with heating oil or residual fuel oil; or to produce electric power by spinning a turbine directly or by creating steam to spin a turbine. In addition, of course, oil products may be used as a raw material (a "feedstock") to create petrochemicals and products, such as plastics, polyurethane, solvents, and hundreds of other intermediate and end-user goods (U.S Energy Information Administration, Independent Statistics and analysis).

However, the amount of crude oil has decreased since last few decades due to high demand, large consumption and inefficient separation of crude oil. According to Saudi Arabic Marketing Informations Resource and Directory (SAMIRAD) the total consumption of crude oil has increased to 84.1 Million Barrel per Day on 2009, compared to 79.4 Million Barrel per Day on 2003. Scientists in Kuwait carried out a study in American Chemical Society (ACS) Energy & Fuels predicted that world conventional crude oil production will peak in 2014 -- almost a decade earlier than some other predictions. Ibrahim Nashawi and colleagues point out that rapid growth in global oil consumption has sparked a growing interest in predicting "peak oil" -- the point where oil production reaches a maximum and then declines. Those cycles can be heavily influenced by technology changes, politics, and other factors. Therefore, the increasing demand of crude oil requires a higher and effective technology to extract and produce large amount of quality crude oil in shorter time.

The crude oil occurs naturally in the form of emulsions, which will cause problems during transportation, processing and storage (Kokal, 2006). According to Lixin et. al. (2003), about eighty percent of exploited crude oils exist in an emulsion state, all over the world. Water and often fine sand and silt are held in various crude oils in permanent emulsions (Leslie & Donald, 1987). Emulsions are two immiscible liquid, whereby one of liquid will become a collection of droplets and dispersed in another liquid phase (Schramm, 1992). Water present as a droplet dispersed in the continuous phase of oil that make crude oil an emulsion, which is difficult to separate. Therefore, various methods have been used to separate the crude oil emulsion to reduce the cost of production and increase the quality of crude oil emulsions.

Separation of oil and water from emulsified solutions, in the process termed demulsification, indicates breakage of the emulsified film surrounding oil or water droplets to allow coalescence or gravitational settling of the oil (Schramm, 1992). Conventionally, demulsification has been achieved by heating and addition of chemicals. Several alternative methods of demulsification have been proposed; these include chemical destabilization with dissolved air flotation (Al-Shamrani et al., 2002), membrane-associated processes (Benito et al., 2001), freezing and thawing (Chen and He, 2003) and (Rajakovic and Skala, 2006), electrical systems (Eow et al, 2001), ultrasonication (Ye, 2008), and microwave irradiation (Chan and Chen, 2002). Among these methods, microwave irradiation is considered effective in demulsification owing to the rapid heating caused by molecular friction and rotation.

1.2 Problem statement

This natural occurring water in oil emulsions have been identified as largely responsible for the stability of these emulsions (Lixin et al., 2003). The water in crude oil (w/o) emulsions is often very stable due to the presence of an interfacial network surrounding the water droplets (Lawrence & Killner, 1948; Blakey & Lawrence, 1954). Nevertheless, stable w/o emulsions have been generally found to exhibit high interfacial viscosity and elasticity modulus (Christophe et al., 2006). The increase in the viscosity of the emulsion will cause problem in transportation and decrease the production rate. Lower viscosity of crude oil with good stability is intended for economic pipeline transportation over large distance.

Other than that, crude oil emulsions also caused some other problem during transportation and processing. The presence of water droplets in the oil will cause corrosion to the pipeline during transportation of the crude oil. It also caused deposition of impurities along the pipeline along transportation. For economic and operational purposes, it is necessary to separate the water completely from the crude oils before transporting or refining them. Minimizing the water levels in the oils can reduce pipeline corrosion and maximize pipeline usage (Harris, 1996; Taylor, 1992).

However, conventional heating methods such as hot plate heating to separate crude oil emulsion needs excessive heating, chemical addition and high residence time (Lemos. R. C. B. et. al., 2010). These increase the cost of production and also will pollute the oil without proper chemical selections.

1.3 Research Objectives

1. To study the stabilization and destabilization of water-in-oil emulsions (w/o) via Microwave Heating Technology.

1.4 Research Questions

1. What are the characteristics in terms of physical properties and chemical properties and stability of crude oil with different w/o ratio?
2. How to separate water-in-crude oil (w/o) emulsion via microwave heating effectively with different microwave penetrating power?
3. Among the conventional methods and microwave heating, which is the most effective way to separate water- in-crude oil (w/o) emulsion?

1.5 Scope of studies

The main objective of this research is to separate water-in-oil in crude oil emulsion. The final product will have two phases which consist of water and oil. In order to obtain the result, we have limited our research within a scope which consists of:

1. Characterization of emulsions in terms of physical and chemical properties.
2. Examination of demulsification of emulsions by conventional methods, which is gravitational separation.
3. Examination of demulsification of emulsions by microwave heating technology.
4. Investigation on the effect of temperature distribution at different locations of irradiated emulsions.
5. Investigation on the effect of varying microwave power generation (360 watts, 540 watts, and 720 watts) on demulsification of emulsions.

1.6 Significance of studies

Separation of water-in-crude oil emulsion via microwave heating is a new concept compared to the conventional method of separation. Microwave heating is a more effective separation whereby previous studies show that this method is able to separate w/o emulsion more effectively and in shorter time. In this research, we are also to investigate the effect of varying microwave power generation on the characteristics and temperature distribution of the irradiated emulsions.

Therefore, a study in this will able to increase the production rate of crude oil. Other than that, effective separation of crude oil able to decrease the corrosion in pipeline and also deposition of impurities in the pipeline along the crude oil transportation. Microwave heating is also an environmentally friendly method whereby no chemical used during the separation. Therefore, no hazardous waste produced along the separation and the oil produced is safe for usage.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

A review of the literature was performed to identify the previous studies performed and identify the studies related to topic. The main sources used are Encyclopedia of Chemical Technology, Emulsions in the petroleum Industry by Schramm, Emulsions and Oil Treating Equipment by Steward & Arnold, Petroleum Engineering Handbook edited by Lake, et al. and some journals of previous research related to this field. The literature will be divided into four main themes: Crude Oil Emulsions; Stability of Crude Oil Emulsions; Separation of Crude oil Emulsions; and Microwave Heating Technology.

2.2 Crude Oil Emulsions

In oil production, oil and water are two mutually immiscible liquid. When oil and water are produced from a well, some organic and inorganic materials also present as contaminants in the fluid stream. These contaminants are absorbed on the interfaces between oil and water phases and form a layer of film that impedes the coalescence of water droplets. Along the way to well bore, up the tubing and through surfaces chokes, agitation occurred, which is sufficient to disperse on liquid as fine droplets and thus make a very good condition of forming a crude oil emulsions (Stewart. & Arnold, 2009).

Emulsions are two immiscible liquids which are brought to contact with each other in a container with sufficient mixing (Kokal, 2006) and one of the two phases will become a collection of droplets that dispersed in the continuous phase of the other liquid (Calderon et al., 2007). Examples of emulsions which we can see in our daily life are milk, mayonnaise, creams and lotions. There are two types of emulsions, which are:

i. Oil-in-water (o/w) - Oil droplets dispersed in continuous phase of water
ii. Water-in-oil (w/o) – water droplets dispersed in continuous phase of oil

During crude oil production, there are several sources of mixing or amount of shear such as flow through reservoir rock, flow through flow lines, fittings and valves which are difficult to avoid (Kokal, 2006). Most of the emulsions present in the form of water-in-oil (w/o) emulsions. Water droplets are dispersed in continuous phase of oil. Water present as the dispersed phase (internal phase) whiles the oil present as the continuous phase (external phase) (Stewart & Arnold, 2009). However, in some cases, crude oil emulsions also present in the form of oil-in-water (o/w).

2.3 Stability of Crude Oil Emulsions

According to Stewart & Arnold, K. (2009), a stable emulsion formed when the water droplets will not settle out of oil phase. As a consequence of small droplet size and presence of an interfacial film on the droplets, a stable dispersion of emulsions formed (Schramm, 1992). The thin film prevents the suspended water droplets from flocculate and coalesces.

2.3.1 Factor Affecting Stability of Crude Oil Emulsions

2.3.1.1 Difference in density between the water and oil phases

Density difference between oil and water phases is one of the factors that determine the rate of which water droplets settle through the continuous oil phase. The greater the difference in density, the more quickly water droplets will settle through the oil phase. Thus, the greater the difference in density between the oil and water phases, the easier the water droplets will settle.

2.3.1.2 Temperature

Temperature affects the physical properties of oil, water, interfacial films and surfactants solubility in oil and water phases will directly affect the stability of emulsions (Kokal, 2006). The most significant effect of temperature is on the viscosity of emulsions because viscosity decreases with increase in temperature.

Temperature will also affect the solubility of surfactant. During phase inversion temperature (PIT), the surfactant loses its solubility in the water and oil phases and thus affected hydrophile-lipophile balance (HLB). Thus, the emulsions tend to invert from water-in-oil to oil-in-water when temperature increases.

2.3.1.3 Size of Water Droplets

The size of the dispersed water droplets affects the rate at which water droplets move through the oil phase. The larger the water droplet, the easier flocculation and coalescence take place. Thus, the water droplets will settle out of oil phase faster. Smaller average size distributions of dispersed water droplets represent tighter emulsions and require longer residence time to separate (Kokal, 2006). The droplet size in an emulsion is highly dependent on the degree of agitation of the emulsions.

2.3.1.4 Viscosity

Viscosity of emulsions is usually higher than that of water and oil because emulsions show non-Newtonian behavior (viscosity is a function of shear rate). Viscosity of emulsions are affected by viscosities of water and oil, volume fraction of water dispersed, droplet size distributions, temperature, shear rate and amount of solids present (Kokal, 2006). However, viscosity is significantly affected by temperature. When temperature increases, viscosity of the emulsions decreases. According to Stoke's Law, when velocity of water droplets increases (due to increase in temperature), viscosity decreases more significantly than the difference in density and thus allow droplet sizes of water increases, indicating coalescence of smaller water droplets forming larger water droplets (Nour, et al., 2010).

2.3.1.5 Interfacial tension

Interfacial tension is the force that holds the surfaces of the water and oil phases together. When the emulsifying agent is not present in two the immiscible liquid, the interfacial tension between water and oil is low. As a result, there is a high probability of coalescence of water droplets and emulsions are said to be unstable.

2.3.1.6 Degree of Agitation

The types and severity of agitation applied to oil-water mixtures determine the size of water droplets. The higher the degree of agitation, the smaller the size of water droplets and thus, added to the stability of emulsions.

2.3.2 Emulsifiers

According to Stewart & Arnold (2009), emulsifiers, also known as emulsifying agent or stabilizer is a material, which has surface active behavior. Some elements in emulsifiers have a preference to the oil, whilst some elements to the water. An emulsifier tends to be insoluble in one of the liquid in emulsion, thus it concentrates at the interface. Paraffins, resins, organic acids, metallic salts, colloidal sites and clays, and asphaltenes are common, naturally occurring surface active material.

Emulsifiers will form a viscous coating on the droplets. This thin film prevents the water droplets to coalescence into larger droplets when they collide. The presence of this film makes the small water droplets take a longer time to settle out from the oil phase-stability added. Emulsifiers may be polar molecules that align themselves around the water droplets. This alignments cause an electrical charge on the surface of the water droplets and since like electrical charges repel, water droplets must collide with sufficient force to overcome the repulsion before coalescence.

2.3.2.1 Surface Active Agent

Surface-active agents (surfactants) are compounds that partially soluble in both phases (water and oil). Surfactants have two parts, hydrophobic part that has affinity to oil phase and a hydrophilic part that has affinity for water (Kokal, 2006). Thus, surfactants have high tendency to concentrate at water/oil interface, and form a thin layer of interfacial film that encapsulates and prevent the water droplets to coalescence. Thus, the water droplets are dispersed in the continuous phase of oil and promote the stability of the emulsions.

2.3.2.2 Finely Divided Solids

Other than surfactants, finely divided solids can act as mechanical stabilizer. The fine solids which are much smaller than dispersed droplets (usually submicron) are collected at the interface of water and oil and are wetted by both water and oil. The very fine solids block the movement of water droplets and prevent them from coagulate and coalescence. However, the effectiveness of the solids highly dependent on particle sizes, interparticle interactions and wettability of the particles (Kokal, 2006).

2.4 Separation of Crude oil Emulsions

Crude oil present as emulsions naturally, even in the crude oil well. However the presence of these emulsions (water-in-oil or oil-in-water) caused the quality of the oil deplete. Therefore, separation needed to separate the emulsion into their respective phase. Three processes are considered in separation: creaming (sedimentation), aggregation, and coalescence (Schramm, 1992). When the emulsion starts to separate, we can observe the oil layer on the top of water with our naked eyes.

2.4.1 Mechanism of Separation

There are there mechanisms involved in separation of emulsions: aggregation, coalescence an sedimentation of creaming. Aggregation is a phenomenon where two droplets become attached to each other at a certain point but are still separated by a thin layer and virtually no change in total surface area or lose their identity. This is also sometimes known as coagulation or flocculation (Schramm, 1992; Kokal, 2006). When more droplets are attached to each other, the individual cluster together and the thin film is retained between them. The thin liquid film will eventually destabilized, burst and form a large single droplet, which known as coalescence (Jacqueline, 1994). The droplet has a size that recognized by naked eyes as a separate phase. Creaming is the opposite of sedimentation and is result from a density difference between two liquid phases.

2.4.1.1 Aggregation or Flocculation

Aggregation or flocculation is a phenomena where droplets clump together, forming aggregates or "flocs". The droplets are close to each other and touch at certain points but there is a film that surrounds the droplets and prevents the droplets to coalescence. When temperature increases, the thermal energy in the water droplets increase and cause the frequency of collisions between water droplets increase thus promote flocculation (Kokal, 2006).

2.4.1.2 Coalescence

Coalescence occurred when small water droplets fused and from bigger droplets. The coalescence rate increases when the frequency of collision increases which can be induced by increasing temperature (Kokal, 2006). Coalescence is a irreversible process and number of water droplets will decrease due to formation of big water droplets from few small water droplets.

2.4.1.3 Sedimentation

Sedimentation or creaming is a phenomenon occurred due to the density difference between two phases. Sedimentation occurred when the water droplets in emulsions settle due to its higher density (Kokal, 2006). Creaming, reverse of sedimentation is used to describe the oil phase, which has lower density rise to the surface of the sample (Schramm, 1992).

2.4.2 Methods of Separation

However, as consequences of small droplet size and presence of interfacial film on the droplet, the emulsion exerts a stable dispersion and it does not settle out by itself and coalesce quickly. Therefore various separation methods are introduced to effectively separate the crude oil emulsions: chemical destabilization with dissolved air flotation (Al-Shamrani et al., 2001), membrane associated process (Benito et al., 2006), freezing and thawing (Chen & He, 2003), electrical system (Eow et al., 2001), ultrasonic (Ye, 2008), microwave irradiation (Chan & Chen, 2002) and other methods or combinations. The conventional method possesses excessive heating, chemical addition and high residence time (Eow & Ghadiri, 2002). Improvement of existing technologies and development of new appropriate method are important to ensure high productivity in crude oil processing.

2.5 Microwave Heating Method

Microwave radiation has been successfully used in many fields of chemistry, including organic synthesis (Cravotto & Cintas, 2007), sample digestion and drying processes (Maichin, 2000). Taking into account the fast energy transfer to irradiated medium, microwaves could be used to perform the demulsification of heavy crude oil emulsions (and, consequently, reducing interferences in further analysis) in a faster way than conventional methods. The microwave demulsification process allows for the destabilization of emulsions, first, by increasing the temperature (it causes a reduction of the continuous phase viscosity and breaks the outer film of drops allowing for the coalescence) and, second, by rearranging the electrical charge distribution of water molecules while rotating them and moving ions around the drops. These two combined effects could result in emulsion breaking without the addition of any chemical agent (Chan & Chen, 2002).

The concept of microwave heating to separate w/o emulsions is first used by Klaila (1983) and shown a positive result. Microwave heating is a different method from other conventional heating method because it make use of electromagnetic waves that penetrate into the molecule and the mechanism of heat transfer took place while other conventional heating transfer heat to the surface of the material. By penetrating heat energy direct into the water molecule, the interfacial thin film in between the small water droplet become destabilized, break and therefore coalescence to form a bigger water molecule. The big water droplet is then separated, where form two layers (oil on top and water at bottom), as the density of oil is much lower than that of water.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This chapter covers the materials, equipments and methods used to solve the problems stated in Chapter 1. Generally, the study is divided into three parts, namely Phase 1: Preparation and formulation of crude oil emulsions; Phase 2: Characterization of the prepared and formulated emulsions in terms of physical and chemical properties; Phase 3: Demulsification of crude oil emulsions via Microwave Heating Technology. Phase 1 is treated as the fundamental phase for undergoing Phase 2 and 3. Phase 1 covers preparation and stabilization of crude oil emulsions using agent-in-oil method with different types of emulsifier and agitation speeds. Phase 2 is the characterization of emulsion formulated whether it is water-in-oil (w/o) or oil-in-water (o/w) from its physical and chemical properties. Phase 3 is a separation of crude oil emulsions formulated using Microwave Heating Technology at different microwave power generation.